Retention of Mechanical Properties After Water Immersion for Glass-Fibre Polymer Composite Laminates with Thermosetting & Thermoplastic Infusible Resins

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INTEGRAL COMPOSITE SHIP

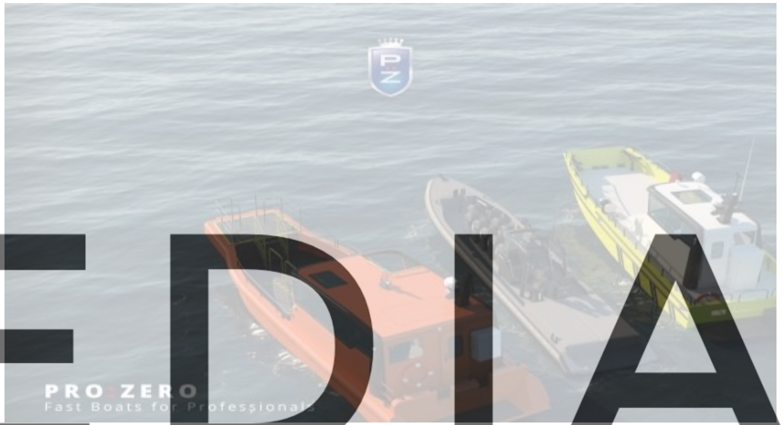
OLLSCOIL LUIMNIGH

Outline

- Overview of FIBRESHIP H2020 project
- Context & Objectives of this study
- Experimental Details
- Results & Discussion
- Conclusions
- Acknowledgements

Challenge

- Fibre-reinforced polymer (FRP) composites dominate shipbuilding in small-to-medium length vessels (< 50 m)
- FRP uptake in ships > 50 m has not transpired – restricted to secondary structures
- Limiting factors: international shipping regulations & vessel certification rules
- Main issues: safety & fire
- The trend in aviation demonstrates that extensive adoption of FRP composite technology in primary and secondary structures is feasible



Courtesy of Tuco Marine (FIBRESHIP partner) – ProZero range of offshore/patrol/service FRP vessels (8-18 m)

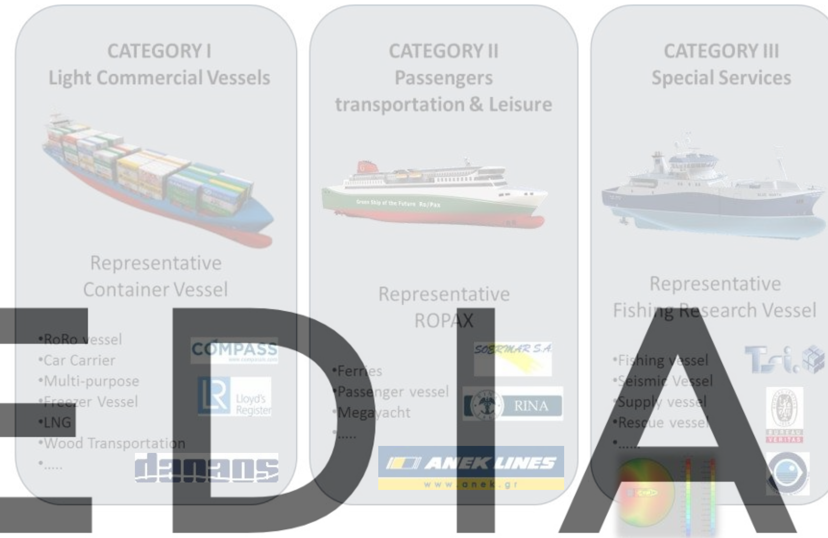
- **Can a research project on the feasibility of designing and building large-length ships from FRP composites help to:**
    - Enhance acceptance of wide FRP usage in primary structures of ships > 50 m
    - Recommend relevant changes in rules and regulations to the responsible bodies
    - Create a niche market opportunity for the manufacture of such ships in the EU

Aircraft	% composite	Length (m)	Fuselage diameter (m)
Boeing 787	50	57-68	5.9
Airbus 350XWB	53	67-74	6.0

Source: Ref.1

Response: FIBRESHIP

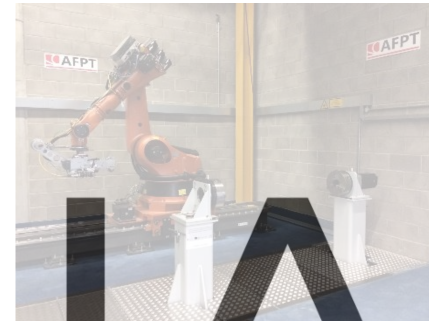
- **Engineering, production and life-cycle management for the complete construction of large-length FIBRE-based SHIPs**
- 18 partners, 11 countries
- European shipyards: 4
- Naval architect/design/engineering companies: 4
- Ship owners & operators: 4
- R&D organisations: 4
- Classification/certification bodies: 3
- Total budget: 11.0M€; EU contribution: 8.7M€
- **UL/IComp budget: 0.72M€**
- Coordinator: TSI SL, Spain
- Duration: 36 months from June 2017
- UL PI: Dr Anthony Comer
- UL co-PI/PM: Dr Ioannis Manolakis
- www.fibreship.eu
- http://cordis.europa.eu/project/rcn/210787_en.html

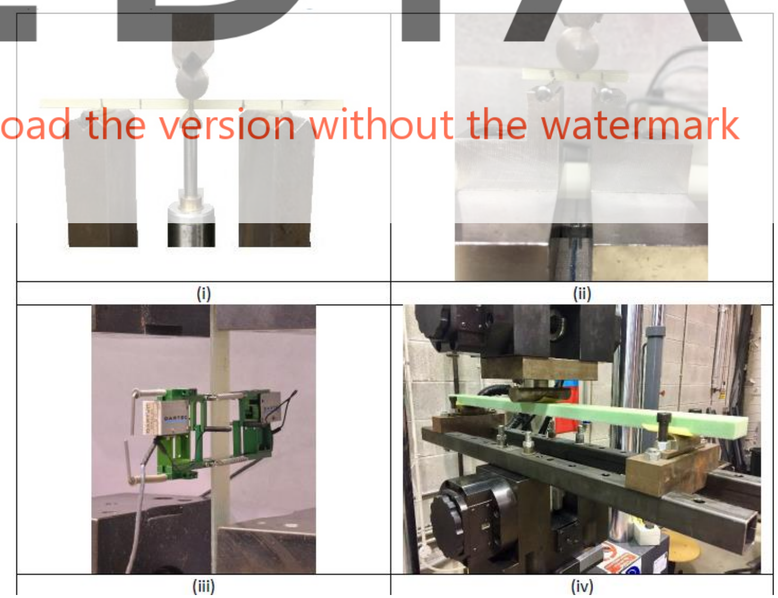


Our role in FIBRESHIP

FIBRESHIP
INTEGRAL COMPOSITE SHIP

- Down-selection of constituent materials (resins, reinforcements, cores etc.)
- Manufacturing of laminates and sandwich's using relevant techniques: VaRTM, ATP
- Material characterization (e.g. mechanical including static and fatigue, thermo-mechanical, environmental)
- Input in Production, Large-scale Validation, Dissemination & Exploitation (task leaders in academic dissemination)
- Team consists of one postdoctoral researcher (Dr Niamh Nash) and two research engineers (Mr Carlos Bachour, Mr Alex Portela)





Context & Objectives

- Matrix of relevant resins compatible with VaRTM
  - Several state-of-the-art thermosetting resins
  - One novel infusible thermoplastic resin (Elium 150, Arkema)
  - One bio-epoxy (SuperSap CLR from Entropy)

- Multi-stage down-selection of resins and reinforcements
  - Several performance criteria (e.g. mechanical & environmental properties, fire performance, cost)

- The current study is an extract from this work
  - Retention of Mechanical Properties after Water Immersion for Glass-Fibre Polymer Composite Laminates with Thermosetting & Thermoplastic Infusible Resins

  - *Which infusible thermosets/thermoplastics are viable solutions for shipbuilding and the marine sector?*

Experimental Details

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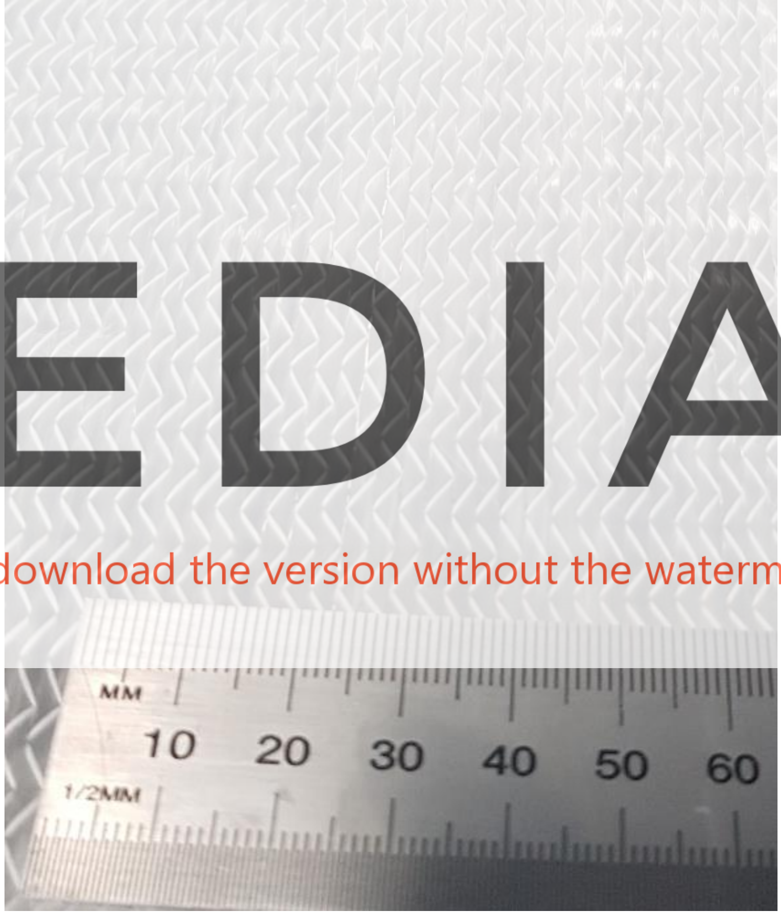
Table 1 VaRTM manufacturing details for composite laminates

#	Class	Resin	Curing agent (s) (w/w)	Viscosity[a] (cP)	Tool	Infusion time / Temp (min/°C)	Curing Schedule	Post-cure schedule
1	Urethane Acrylate	CRESTAPOL 1210	100:2:1:1[b]	175 cP @ 25°C (neat resin)	Glass	11/21.1	1h at RT	Not required
2	Epoxy	SR1125	100 : 14[c]	680 cP at 20°C 305 cP at 30°C 160 cP at 40°C	GLASS (+ heated Mat)	40/19.9	16 hrs @ 40°C	8 hrs @ 80°C
3	Bio-epoxy	SUPER SAP CLR	100:33[d]	300 cP @ 25°C	Aluminum (heated)	92/35	Overnight at RT	2 hrs @ 120°C
4	Phenolic	CELLOBOND J2027X	100:4[e]	270cP @ 25°C	Aluminum (heated)	36/60	15 mins @ 60°C	3hrs @ 80°C
5	Acrylic (TP)	ELIUM 150	100:2.5[f]	100 cP @ 25°C (neat resin)	Glass	23/21.9	Overnight at RT	Not required

[a] values from TDS; [b] 2 parts by weight of accelerator D (10% solution of dimethyaniline in styrene): 1 part by weight of accelerator G (1% cobalt solution in styrene): 1 part by weight of peroxide catalyst (Trigonox 44B); [c] SD3303; [d]INS slow hardener; [e]Phencat 382 [f]Benzoylperoxide Luperox A40FP-EZ9

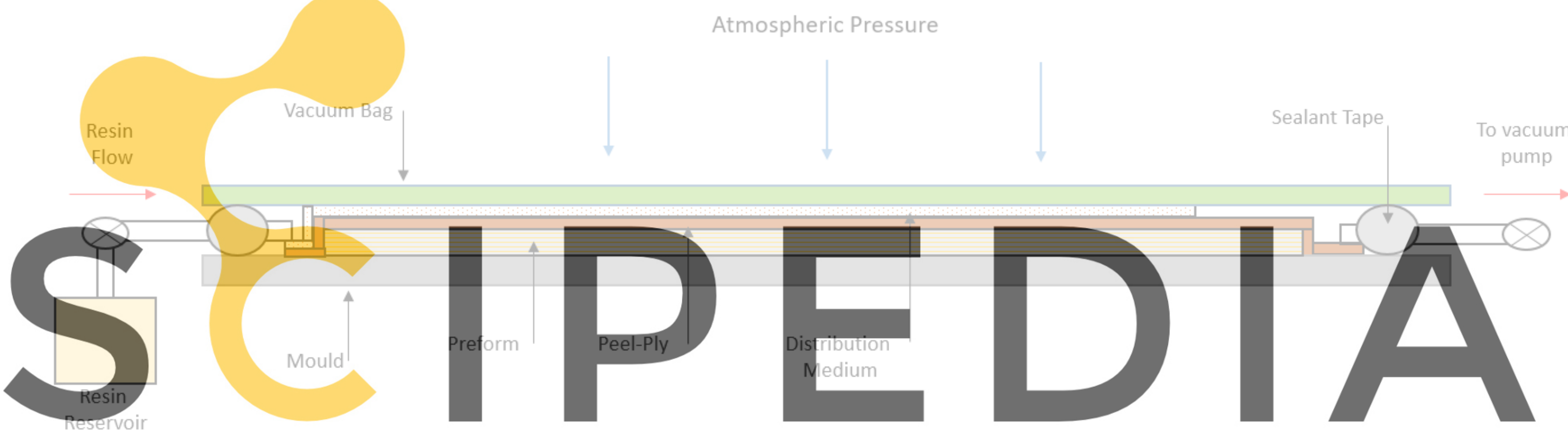
Experimental Details

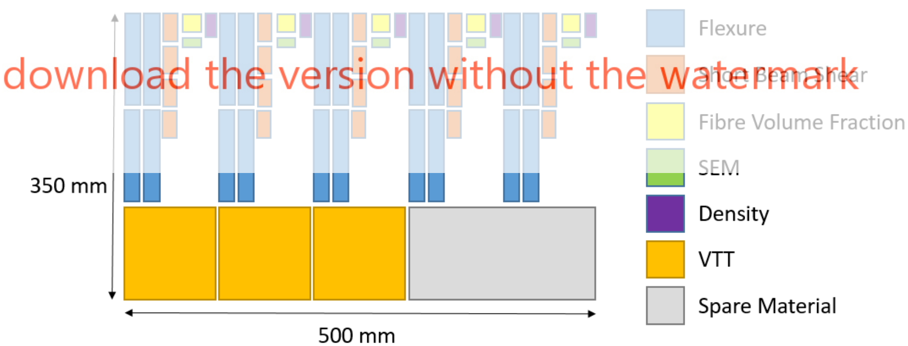
- Non-crimp-fabric from Saertex used for all laminates manufactured
- E-glass 0°: 898 gsm
- E-glass 90°: 81 gsm
- Polyester stitching: 17 gsm
- Total: 996 gsm
- Sizing: Silane
- Lay-up: 0_{2S} (4 layers of NCF in a UD configuration)



Glass fibres
SAERTEX U-E-996 g/m^2

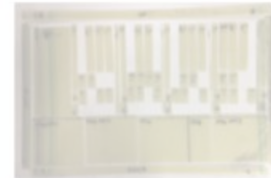
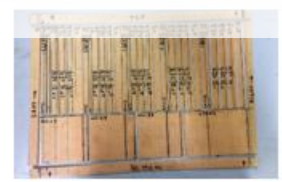
Experimental Details





- Laminates are manufactured on either a glass (see image) or heated aluminium tool
- Approach is suitable for manufacture of large components

Experimental Details

1	Urethane Acrylate V_f = 57±0.3%		
2	Epoxy V_f = 58±3.0%		
3	Bio-epoxy V_f = 60±0.6%		
4	**Phenolic** V_f = 58±0.4%		
5	**Acrylic (TP)** V_f = 56±1.0%		

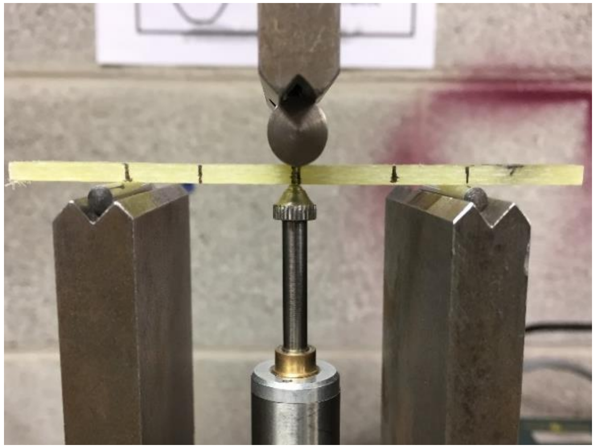
All laminates nominally: 350 x 500 x 3 mm

Experimental Details

Test	Standard	Properties	Nominal Sample Dimensions	Number of Samples
INTERLAMINAR SHEAR (ILS)	ISO 14130	APPARENT INTERLAMINAR SHEAR STRENGTH	30 mm X 15 mm X 3 mm	5 No immersion 5 After immersion
FLEXURE – 3 POINT BEND	ISO 14125	FLEXURAL STRENGTH FLEXURAL MODULUS	80 mm X 15 mm X 3 mm	5 No immersion 5 After immersion
FIBRE VOLUME FRACTION	ISO 14127 ASTM D3171	FIBRE VOLUME FRACTION	20 mm X 20 mm X 3 mm	5

Immersion Bath (Deionised water @ 35 °C)

Apparent Interlaminar Shear Strength by Short Beam Shear



Flexural Strength and Modulus by 3 point bend

Results & Discussion

Table 2. Interlaminar shear strength (ILSS) of various laminates in dry and wet condition (28 days @ 35°C). All laminates manufactured with glass NCF

#	*Class*	*Resin*	*Apparent ILSS* (No Immersion) (MPa)	*Apparent ILSS* (After Immersion) (MPa)	*% Change in Apparent ILSS after immersion*	*Moisture uptake average (mg)*
1	Urethane Acrylate	CRESTAPOL 1210	42.0 (±3.0%)	39.8 (±9.0%)	-5.2 %	5.7
2	Epoxy	SR1125	50.5 (±1.7%)	51.8 (±1.7%)	2.6 %	11.2
3	Bio-epoxy	SUPER SAP CLR	57.7 (±3.6%)	54.5 (±5.0%)	-5.5 %	5.9
4	Phenolic	CELLOBOND J2027X	33.5 (±4.8%)	35.7 (±8.5%)	6.6	40.5
5	Acrylic (TP)	ELIUM 150	56.8 (±3.6%)	34.9 (±12.5%)	-38.6 %	21.7

Minimum required laminate property values in accordance with Lloyds register materials and qualification procedures for ships book K procedure 14-1 and 14-2. Revision 01 Dec 2013: ILSS at least 15 MPa;

Maximum allowed property drop from the dry state is 25%
Maximum allowed water uptake is 70 mg over 7 days

Results & Discussion

Table 3. Flexural strength of various laminates in dry and wet condition (28 days @ 35°C). All laminates manufactured with glass NCF

#	*Class*	*Resin*	*Flexural Strength* (No Immersion) (MPa)	*Flexural Strength* (After Immersion) (MPa)	*% Change in Flexural Strength after immersion*	*Moisture uptake average (mg)*
1	Urethane Acrylate	CRESTAPOL 1210	790 (±11.3 %)	755 (±6.0 %)	-4.4 %	22.4
2	Epoxy	SR1125	853 (±8.5 %)	812 (±2.0 %)	-4.9 %	40.8
3	Bio-epoxy	SUPER SAP CLR	865 (±8.9 %)	796 (±8.0 %)	-8.0 %	78.7
4	Phenolic	CELLOBOND J2027X	858 (±6.7 %)	858 (± 3.0 %)	0.0 %	140.5
5	Acrylic (TP)	ELIUM 150	942 (±3.8 %)	734 (±13.0 %)	-22.1 %	34.4

Minimum required laminate property values in accordance with Lloyds register materials and qualification procedures for ships book K procedure 14-1 and 14-2. Revision 01 Dec 2013: flexural strength and flexural modulus for a laminate with equivalent fibre mass fraction (0.72) at least 367 MPa and 19.5 GPa respectively

Maximum allowed property drop from the dry state is 25%
Maximum allowed water uptake is 70 mg over 7 days

Results & Discussion

Table 4. Flexural modulus of various laminates in dry and wet condition (28 days @ 35°C). All laminates manufactured with glass NCF

#	*Class*	*Resin*	***Flexural Modulus*** (No Immersion) (MPa)	***Flexural Modulus*** (After Immersion) (MPa)	***% Change in Flexural Modulus after immersion***
1	Urethane Acrylate	CRESTAPOL 1210	34.5 (±2.0 %)	32.5 (±12 %)	-5.8 %
2	Epoxy	SR1125	30.3 (±8.1 %)	31.0 (±3.0 %)	2.3 %
3	Bio-epoxy	SUPER SAP CLR	32.8 (±3.8 %)	29.7 (±9.0 %)	-9.5 %
4	Phenolic	CELLOBOND J2027X	34.9 (±4.1 %)	33.0 (±7.0 %)	-5.4 %
5	Acrylic (TP)	ELIUM 150	33.8 (±1.6 %)	34.0 (±12.0 %)	0.6 %

Minimum required laminate property values in accordance with Lloyds register materials and qualification procedures for ships book K procedure 14-1 and 14-2. Revision 01 Dec 2013: flexural strength and flexural modulus for a laminate with equivalent fibre mass fraction (0.72) at least 367 MPa and 19.5 GPa respectively

Maximum allowed property drop from the dry state is 25%

Results & Discussion

Table 5. Summary of changes in mechanical properties as a result of immersion in deionized water (28 days @ 35°C). All laminates manufactured with glass NCF

#	*Class*	*Resin*	*Δ ILSS*	*Δ Flexural Strength*	*Δ Flexural Modulus*
1	Urethane Acrylate	CRESTAPOL 1210	-5.2 %	-4.4 %	-5.8 %
2	Epoxy	SR1125	2.6 %	-4.9 %	2.3 %
3	Bio-epoxy	SUPER SAP CLR	-5.5 %	-8.0 %	-9.5 %
4	Phenolic	CELLOBOND J2027X	6.6	0.0 %	-5.4 %
5	Acrylic (TP)	ELIUM 150	-38.6 %	-22.1 %	0.6 %

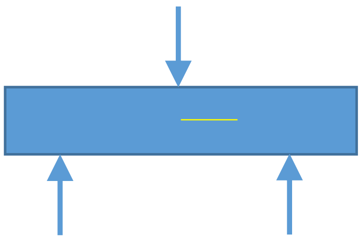
Minimum required laminate property values in accordance with Lloyds register materials and qualification procedures for ships book K procedure 14-1 and 14-2. Revision 01 Dec 2013: flexural strength and flexural modulus for a laminate with equivalent fibre mass fraction (0.72) at least 367 MPa and 19.5 GPa respectively

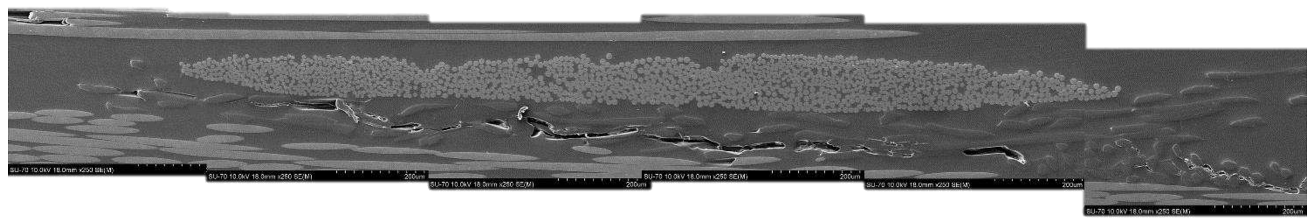
Maximum allowed property drop from the dry state is 25%

Results & Discussion

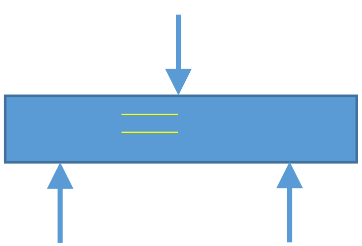
Acrylic (TP): Reduction in ILSS (-38 %) is due to a change in failure mode after immersion !

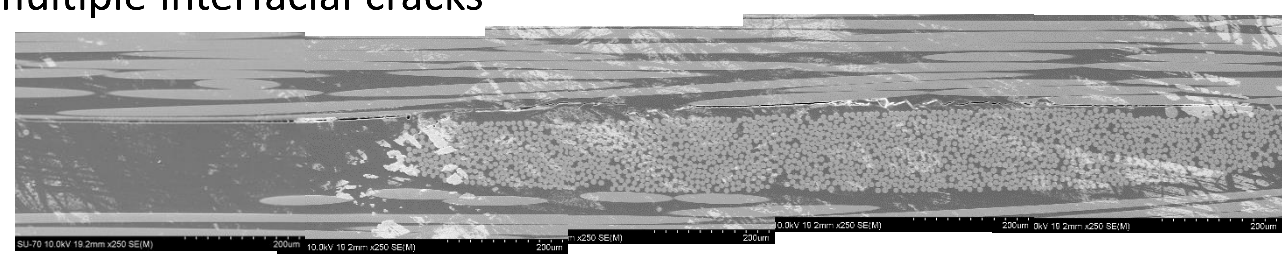
DRY Condition ILS: single non-interfacial crack at mid thickness

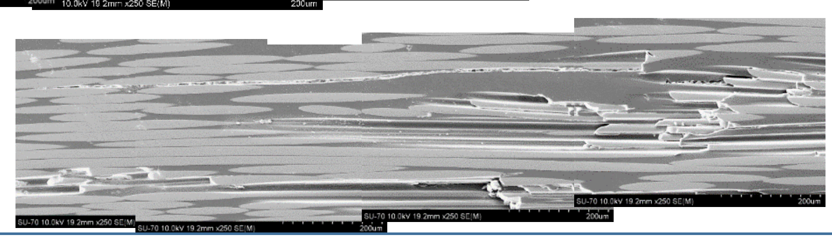




After Immersion ILS: multiple interfacial cracks







Conclusions

Summary: Selected mechanical properties of candidates from various resin classes were evaluated for their suitability in the manufacture of marine vessels (> 50 m). Traditional thermosetting resins systems were included along with some novel infusible options (acrylic thermoplastic and a bio-epoxy).

Mechanical Properties:

- All laminates manufactured comfortably exceeded the minimum requirements set by classification societies in terms of ILSS and flexural properties in the dry condition. Other important properties obviously still need to be addressed such as toughness, impact, fatigue and the effect of thickness.

- Immersion in deionised water had a detrimental affect mainly on the acrylic. A change in failure mode (**non-interfacial to interfacial crack propagation**) was observed. (The others were largely unaffected)

Manufacturing: Elevated temperature infusion and cure is required for the *Phenolic*, *Epoxy* and *Bio-epoxy* which is not very practical for production of large parts in ship yards. Additional issues were noted for the *phenolic* (attacked nylon vacuum membrane, condensation reaction), *bio-epoxy* (very slow infusion) and *urethane acrylate* (uses styrene reactive diluent technology).

Many other factors to be considered including cost, availability, repair…

Acknowledgements

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Thank you for your attention